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THE RELATIONS USED TO ANALYZE THE PHASE EQUILIBRIUM PROPERTIES OF BINARY REFRIGERANT MIXTURES

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ABSTRACT

At present, the method adapted to analyze the phase equilibrium properties of refrigerant mixtures is as follows: Firstly, based on some experimental data of phase equilibrium, the interactive factor between the mixed refrigerants can be derived by using a equation of state. Secondly, the vapour and liquid phase equilibrium properties are predicted by combining the mixed rule with phase equilibrium condition of mixture. Because the value of interactive factor for mixture varies as the different temperature and the concentration, the deviation between the calculated results and measured values is obvious.

In this paper, first of all, the mathematical model of activity-coefficient for the binary refrigerant mixture has been built on the basis of the statistical mechanics theory. Then, the relations used to calculate the phase equilibrium properties of saturated vapour and liquid for binary refrigerant mixture, whose undefined constants were determined by regressing the measured data, have been found. Finaly, some phase equilibrium properties of mixture R12/R115 and R22/R114 have been predicted by using above relations, and the calculated results agreed with the measured values.

1. NOMENCLATURE

r ------- Activity coefficient;
x ------- Mole concentration of component A in liquid phase;
R ------- Gas constant;
T ------- Temperature, K;
N ------- Avogadro's number;
Z ------- Number of neibouring molecule to enclose the mixture molecular;
Q ------- Work needed by neibouring molecular's moving in mixing process;
Tr ------ Reduced temperature;
A, B ----- Component A and B.

2. INTRODUCTION

At present, mixture refrigerant play an important role in

the replacement of CFCs. Thermodynamic properties of mixture is different from pure refrigerant. For example, at a certain concentration, phase-changing process of mixture is an isobatic but nonisothermic one. So, it is difficult to determine the datum (i. e. determining the evaporating temperature and condensing temperature) for comparing the cycle efficiency of refrigerating system. With the concentration of mixture changing, its thermodynamic properties are different and its effect on the heat transfer coefficients of evaporating and condensing process is large. So, it is very necessary to study the phase equilibrium characteristics of vapor and liquid of mixture(i. e. the relation of pressure, temperature and concentration) for analysing other thermodynamic properties of mixture.

The conventional method of studying equilibrium characteristics between vapor and liquid of mixture is: Choosing an equation of state, using experimental data of equilibrium between vapor and liquid of mixture, regressing the interactive factor of two mixed components, finaly, using mixing rule and the conditions of phase equilibrium to predict the properties of equilibrium between vapor and liquid. Because the interactive factors are variant with concentration and temperature, they always make large defference between the calculated results and experimental data of equilibrium between vapor and liquid. In addition to that, it yields errors inevitably to deduce the complex mathematical model in fugacity equation.

From the view of statistical machnics, in this paper, authors deduced the activity-coefficient mathematical model of nonideal liquor for binary mixture, combined with experimental data of phase equilibrium, regressed the constants in the model, finaly, got a more accurater analitic equation of pressure -temperature-concentration for binary mixture under the condition of phase equilibrium. The calculated results and experimental data of R12/R115 and R22/R114 were compared.

3. THEORETICAL MODEL

Margules [1] had put forward an experiential equation of activity coefficients for binary mixture:

$$ln\gamma_A = b\,(1-x)^2 + c\,(1-x)^3 + \cdots\cdots \qquad (1)$$

$$ln\gamma_B = b'\,x^2 + c'\,x^3 + \cdots\cdots \qquad (2)$$

In above equations, b, c, b', c',..... are unknown constants to be determined.

Gibbs- Duhe equation reveals the relation between concentration and activity-coefficient of binary mixture:

$$x \cdot \left[\frac{\partial(\ln\gamma_A)}{\partial x}\right]_{T,p} - (1-x) \cdot \left[\frac{\partial(\ln\gamma_B)}{\partial(1-x)}\right]_{T,p} = 0 \qquad (3)$$

Derivating eq. (1) and eq. (2) and taking them into eq. (3) , the expression of activity-coefficients can be dedued:

$$\left.\begin{aligned}\gamma_A &= EXP\,[b\,(1-x)^2]\\ \gamma_B &= EXP\,[b\,x^2]\end{aligned}\right\} \qquad (4)$$

From the statistical theory of binary mixing procedure, the expression of activity-coefficients can be deduced:

$$\left.\begin{aligned}\gamma_A &= EXP\left[\frac{\omega}{RT}(1-x)^2\right]\\ \gamma_B &= EXP\left[\frac{\omega}{RT}x^2\right]\end{aligned}\right\} \qquad (5)$$

$$\omega = N_c \cdot Z \cdot Q$$

Eq. (5) reveals the molecular properties of constant b in the activity-coefficients expression (i. e. eq. (4)) from microcosm profoundly, i. e. b is determined by the properties of vapor, temperature, number of molecules and moving energy.

In the saturated liquor of nonideal mixture, divided pressure of every component in vapor is:

Divided pressure of component A in vapor:

$$p_A = p_A^0 \cdot \gamma_A \cdot x \qquad (6)$$

Divided pressure of component B in vapor:

$$p_B = p_B^0 \cdot \gamma_B \cdot (1-x) \qquad (7)$$

Taking eq. (5) into eq. (6) and eq. (7), then

$$p_A = p_A^0 \cdot x \cdot EXP\left[\frac{\omega}{RT}(1-x)^2\right] \qquad (8)$$

$$p_B = p_B^0 \cdot x \cdot EXP\left[\frac{\omega}{RT}x^2\right] \qquad (9)$$

From Daolton Law, it can be known that saturated vapor pressure of mixture is:

$$p = p_A + p_B$$

$$= p_A^0 \cdot x \cdot EXP\left[\frac{\omega}{RT}(1-x)^2\right] + p_B^0 \cdot (1-x) \cdot EXP\left[\frac{\omega}{RT}x^2\right] \qquad (10)$$

In above eqiations, P_A^s , P_B^s represent saturated pressure of component A and B in mixture at a same temperature.

The relation between vapor phase concentration y and liquid phase concentration x of component A is expressed by following equation:

$$x = y^m \tag{11}$$

Taking it into eq. (10), then

$$p = p_a^0 \cdot y^m \cdot EXP\left[\frac{\omega}{RT}(1-y^m)^2\right] + p_B^0 \cdot (1-y^m) \cdot EXP\left[\frac{\omega}{RT}(y^m)^2\right] \tag{12}$$

Using eq. (10) and eq. (12), bulb point line and dew point line of mixture can be calculated respectively(As shown in Figure 1.).

4. THE COMPARISON BETWEEN THE RESULTS CALCULATED BY THE REGRESSED RELATIONS AND THE EXPERIMENTAL DATA

In this paper, saturated pressure of several pure refrigerants is calculated by using the four order polynomial. Unknown coefficients a_0 ----- a_4 can be regressed from the data in reference [3]. The regressed values are shown in Table 1.

$$p^s = a_0 + a_1 \cdot T_r + a_2 \cdot T_r^2 + a_3 \cdot T_r^3 + a_4 \cdot T_r^4$$

The comparison between calculated values of saturated pressure by regressed relationship for several kinds of pure refrigerants and those in reference [3] is shown in Table 2.

In this paper, the data of saturated pressure and saturated temperature are measured with various concentration of solution. With these data, the undetermined coefficients in eq. (10), eq. (11) have been regressed in polynomial expression as below:

$$\omega = a + b \cdot T + c \cdot T^2 + d \cdot T^3 + e \cdot T^4$$
$$m = A + B \cdot T + C \cdot T^2$$

The regrssed values of constants in the function of ω, are shown in Table 3.

Taking the regressed values into eq. (11), the dew point line of R115/R12 mixture can be calculated. The range of

temperature changes from 269.15K to 318.15K and mole concentration from 0.0 to 1.0. Comparing the 35 column of values in calculation with that in experiment, one can find that the average deviation is 0.21% and maximum deviation is 2.55%. Figure 2. shows the calculated results and the experimental data when the temperature being 318.15K. It reveals that one is in concord with the other.

Based on the experimental data in reference [4], the expression used to calculate both the dew point line and bulb point line of R22/R114 mixture, has been obtained by regression. The calculated results and the experimental data are compared in Table 4. The average deviation is 0.007%, and the maximum deviation is 1.78%. The agreement of them is very satisfied.

5. CONCLUSION

This paper have deduced the mathematical model of vapor-liquid equilibrium of binary mixture with statistical theory and uncovered the thermodynamic essence of activity- coefficient. By regressing the constants in mathematical model with the experimental data, the temperature- pressure- concentration equation of saturated mixture has been obtained. The calculated values and the experimental data are well fitted.

The phase- graph of binary mixture refrigerant may be conveniently calculated by using this kind of expression. It provided an effective method for researching the characteristics of vapor-liquid equilibrium of binary mixture.

6. REFERENCES

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Table 1. The Regressed Values of $a_0 \sim a_4$ Constants for Several Pure Refrigerants

Regressed Coefficients	R115	R12	R22	R114
a_0	0.1317	-1.626	-2.00	-0.8069
a_1	-3.577	6.878	7.196	1.823
a_2	18.61	-3.944	1.034	7.041
a_3	-35.77	-15.98	-28.48	-24.98
a_4	23.74	18.74	27.17	20.12
Temperature Range (K)	233.15~331.15			

Table 2. The Comparison between the Calculated Values of Saturated Pressure for Seversal kind of Pure Refrigerants and the Values in Reference

Temperature (k)	233.15		333.15	
Working Media	R12	R22	R12	R22
Pressure Value in reference [3] (MPa)	0.06415	0.10527	1.5212	2.4279
Pressure of calculation (MPa)	0.06416	0.10530	1.5211	2.4278
Error %	0.016	0.030	-0.003	-0.006

Table 3. The Regressed Values of R115/R12 Mixture in the Function ω

Coefficients	Regressed Value
a	0.213429×10^{7}
b	-0.2895143×10^{5}
c	0.1471703×10^{3}
d	-0.3320757
e	0.2805883×10^{-3}

Table 4. Comparing Between the Calculated Values of Dew Point and Experimental data for R22/R114

Temperature (K)	R22 Mole Concentration	Pressure in reference[4] (MPa)	Calculated Pressure (MPa)	Error %
253.15	0.3829	0.059	0.058	1.41
	0.9555	0.2193	0.2179	0.63
293.15	0.5098	0.3341	0.3308	0.98
	0.8550	0.6511	0.6570	-0.90
333.15	0.2360	0.7322	0.7314	0.11
	0.9575	2.225	2.2640	-1.78

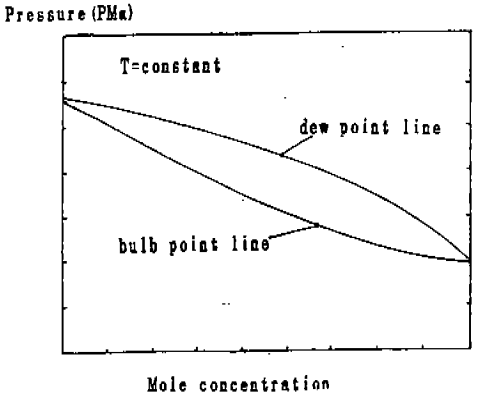

Figure 1. Phase-graph of non-azeotrope dinary mixture

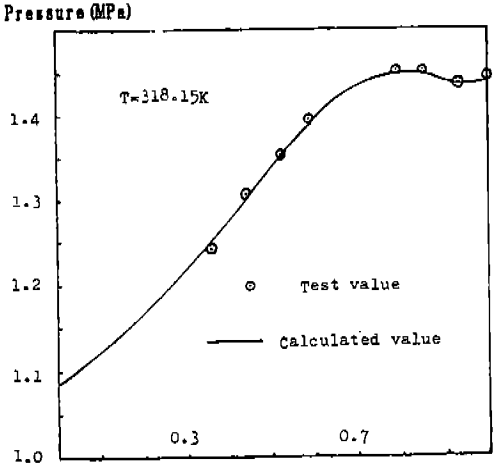

Figure 2. Comparison of the values of R116/R12 dew point line in calculation and experiment